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The Verwey phase of magnetite – a long-running mystery in magnetism**

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Abstract:
Magnetite (Fe_3O_4) is the original magnetic material and the parent of ferrite magnets, with modern applications ranging from spintronics to MRI contrast agents. At ambient temperatures magnetite has a cubic spinel-type crystal structure, but it undergoes a complex structural distortion and becomes electrically insulating below the 125 K Verwey transition. The electronic ground state of the Verwey phase has been unclear for over 70 years as the low temperature structure was unknown, but the full superstructure was recently determined by high energy microcrystal x-ray diffraction. An analysis of 168 frozen phonon modes in the acentric (and hence multiferroic) low temperature magnetite structure is presented here. Differences between the amplitudes of centric and acentric branches of, X and W modes all contribute to the significant off-center atomic distortions in the low temperature structure.

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Keywords:
magnetite, Verwey transition, multiferroic

I. INTRODUCTION

Magnetite (Fe_3O_4) is the mineral that gave rise to the discovery of magnetism. In the AB_2O_4 spinel-type structure of magnetite, there are twice as many octahedral *B*-site Fe^{3+} $3d^5$ $S = 5/2$ up-spins as there are down-spins at the tetrahedral *A* sites, resulting in a net magnetization below the 858 K Curie transition. Rapid hopping of an 'extra' down-spin electron between *B* sites, as represented in the formal charge distribution $Fe^{3+}[Fe^{2.5+}]_2O_4$, results in minority-spin-polarised electronic conductivity. The Verwey transition, at which magnetite undergoes a structural distortion and becomes electrically insulating, was observed in measurements of heat capacity, conductivity, magnetisation and many other properties at around 125 K [1,2]. A complex lattice distortion to a monoclinic $\sqrt{2}$ x $\sqrt{2}$ x 2 superstructure of the cubic room temperature spinel lattice was later identified [3,4]. The supercell has *Cc* space group symmetry and contains 224 atoms. Verwey proposed that the transition is driven by a regular condensation of Fe^{2+} and Fe^{3+} ions equivalent to localisation of the minority spin 'extra' electrons [1], a phenomenon now known as 'charge ordering' that has been verified in many other oxides [5]. However, the ground state of magnetite has remained a contentious issue for over 70 years, as microtwinning of *Cc* domains below the Verwey transition hampers diffraction studies of the low temperature structure. Recent partial structure refinements from powder diffraction data [6,7,8] and Fe K edge resonant X-ray diffraction studies [9,10,11] have shown some evidence for charge order.

An X-ray refinement of the full low temperature *Cc* superstructure of magnetite was recently reported [12]. Fe^{2+}/Fe^{3+} charge ordering and Fe^{2+} t_{2g}-orbital ordering was evidenced from analysis of the local distortion modes of the BO_6 octahedra, in agreement with predictions from some electronic structure calculations [13,14], and showing that Verwey's hypothesis is correct to a useful first approximation. However, additional structural distortions in which *B*-*B* distances within linear Fe-Fe-Fe units are anomalously shortened suggested that the 'extra' down-spin electrons are not fully localised as Fe^{2+} states, but are instead spread over three sites resulting in highly structured three-site

polarons termed ‘trimerons’. Electronic structure calculations for the experimental *Cc* structural model support the first-approximation charge and orbital order model, and also the fuller trimeron description [15]. The apparent dominance of trimeron order within the Verwey structure of magnetite was not proposed in previous theoretical or experimental studies.

In this paper we present further analysis of the frozen lattice modes in the low temperature magnetite structure that follows on from the description of the experimental structure [12]. This shows that the pseudosymmetry models in previous studies do not provide a good approximation to the *Cc* structure, in particular because substantial off-center distortions result from all the main frozen phonon classes. Coupling of the resulting ferroelectric polarisation to the magnetization may lead to multiferroism in the Verwey phase of magnetite.

II. EXPERIMENTS AND DISCUSSION

The crystal structure of magnetite at 90 K was determined from a synchrotron microcrystal diffraction experiment as described elsewhere [12]. The low temperature *Cc* crystal structure has 168 variable (*x,y,z*) atomic coordinates, of which 166 are independent and two fix the cell origin. Visual appreciation of the structural distortions is not easy, as shown by Fig. 1, and it is more useful to describe the coordinate shifts by 168 equivalent phonon amplitudes. 80 modes are required for the closest centric description (preserving spatial inversion symmetry) in space group *C2/c*, and an additional 88 are needed for the full acentric *Cc* description. Only one displacement (the O-atom Γ_{1+} mode) is present in the high temperature cubic structure and the remainder all freeze at the 125 K Verwey transition.

Distortion mode analysis of the *Cc* structure with respect to the high temperature $Fd\bar{3}m$ cubic structure was performed with the aid of the ISODISPLACE program [16]. A summary of the space groups for which the reconstructed modes form primary order parameters (POP) is given in Fig. 2.

These are always type 1 maximal non-isomorphous subgroups of $Fd\bar{3}m$ if they belong to the Γ point, and of type 2 if they arise due to Δ, X, or W point distortions. Many of the pseudosymmetry candidates used in previous refinements (e.g. $R\bar{3}m$, *Pmca, C2/c*) do not appear as their corresponding POPs are already branched in this mode analysis leading to subgroup symmetries of these candidate space groups.

The amplitudes for the four classes of frozen phonon are shown in Fig. 3. The Γ-point amplitudes are very small so a structural model using only some of these modes, such as a rhombohedral approximation, does not lead to a realistic description. In rhombohedral $R\bar{3}m$ symmetry [17] the branched $\Gamma_{5(a)}$ and $\Gamma_{5(b)}$ amplitudes would be equivalent, and although this is approximately true, the relatively large magnitude of the Γ_3 modes (describing pseudo-tetragonal distortion) and the substantial Δ, X and W point amplitudes show that this is not a useful pseudosymmetry approximation.

A *Pmca* $1/\sqrt{2}$ x $1/\sqrt{2}$ x 2 subcell approximation was used in partial structure refinements [4,6,7]. The centric *Pmca* space group has the irreducible representations Γ_1, Γ_3, Γ_5, Δ_5 and X_1 and so is not one of the subgroups implied by a POP of $Fd\bar{3}m \rightarrow Cc$ in Fig. 2, as the inversion center has already been lost in the Γ-point. Nevertheless, by comparing the different branches of the POPs, it is possible to ascertain the degree of pseudosymmetry with respect to *Pmca*. Fig. 3 shows that the Δ_5 modes have large amplitudes while those for Δ_2 and Δ_4 are much smaller, making *Pmca* an apparently good subcell approximation. The inequivalence of centric $\Delta_{5(a)}$ and acentric $\Delta_{5(b)}$ branch amplitudes leads to off-center distortions of magnitude 0.05–0.10 Å, and these are captured by lowering the subcell symmetry from *Pmca* to $Pmc2_1$ [4]. However, the *Pmca* and $Pmc2_1$ approximations neglect the X_2, X_3, X_4 and W point modes, all of which have substantial amplitudes, as well as the branching of the X_1 modes shown in Fig. 3. Large differences between the magnitudes of the centric and acentric X_1 modes are apparent, so the net effect is a significant off-center distortion of the *B*-site Fe and the O atoms.

The closest centric pseudosymmetry approximation to the Cc structure is provided by space group *C2/c* [8]. Here the magnitudes of the (a) and (b) branches of the W point phonons must be identical.

However, Fig. 3 shows that the magnitudes of many of the branched W phonon pairs are quite unequal, leading to net off-center displacements of up to 0.06 Å, so that even the *C2/c* monoclinic description is a poor approximation to the final structure.

III. CONCLUSION

Symmetry mode analysis of the low temperature magnetite structure shows that attempts to describe the structure in terms of a few frozen phonons or a collection of sub-symmetries do not lead to good overall approximations. Although some modes such as Δ_5 and X_4 have large amplitudes, consistent with spectroscopic measurements on the cubic phase, they are not unique primary order parameters for the Verwey transition. The orthorhombic *Pmca* and $Pmc2_1$ subcell approximations capture the magnitude of the Δ modes fairly well. Differences between the amplitudes of centric and acentric branches of Δ, X and W modes all contribute to the significant off-center atomic distortions in the *Cc* magnetite structure. Hence the Verwey phase is confirmed as being ferroelectric, and coupling of the electric and magnetic polarisations is expected to lead to multiferroic properties.

ACKNOWLEDGEMENT

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Figure Captions.

Fig. 1. (Color online) Views of the AB_2O_4 magnetite structure with the *Cc* supercell and axes shown and Fe/O sites as large (*A* blue and *B* green)/small (red) spheres. Images from left to right show the structure with the 168 displacement amplitudes multiplied by 0 (equivalent to the high temperature

regular spinel structure), by 1 (the experimental 90 K structure), and by 4 (exaggerating the 90 K distortions for visual effect).

Fig. 2. (Color online) Descent of space group symmetry from $Fd\bar{3}m$ to Cc for the Verwey superstructure of magnetite. Arrows represent symmetry descents. The space groups for which distortion modes (irreducible representations) form POPs (the kernels of the irreducible representations) are shown in bold (red) boxes, along with the k-points, order parameter directions, and mode branch labels. Additional space groups in which the POPs are not branched are also shown.

Fig. 3 (Color online) Plots of the amplitudes for the four classes of frozen phonons (Γ, Δ, X, and W point distortions) in the 90 K magnetite structure, following the scheme of Fig. 2 in ref. 12. The branching of modes is indicated by (a), (b), etc.

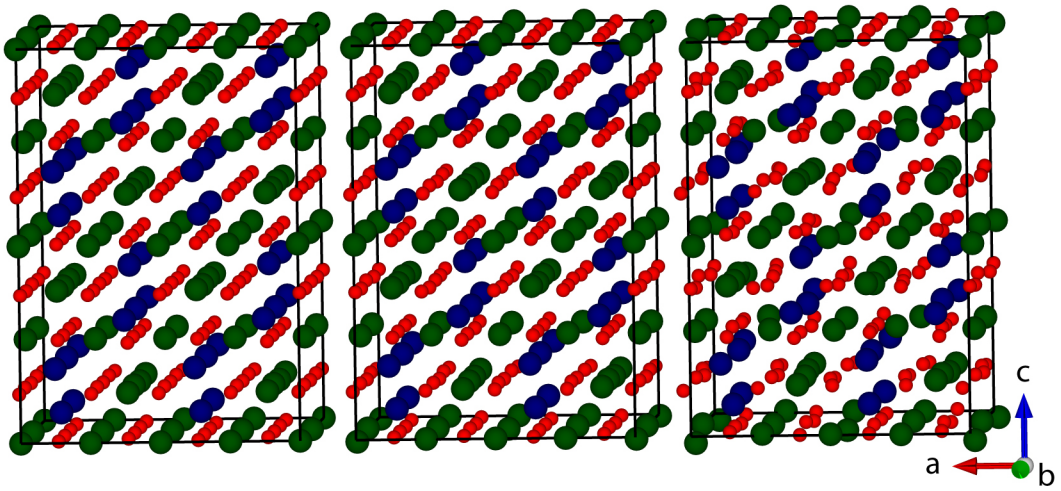
c
a
b

Fig. 1.

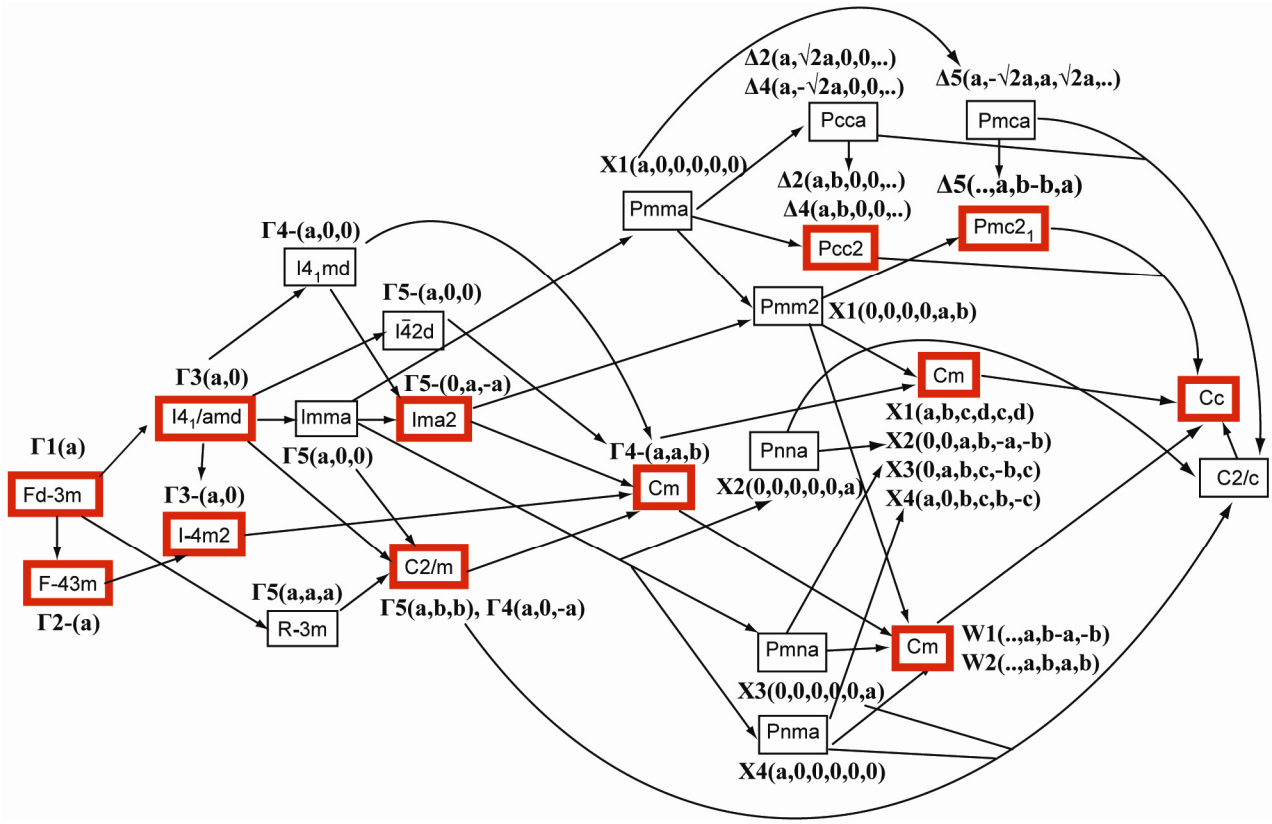
Δ2(a,√2a,0,0,..)
Δ4(a,-√2a,0,0,..)
Δ5(a,-√2a,a,√2a,..)
Pcca
Pmca
X1(a,0,0,0,0,0,0)
Δ2(a,b,0,0,..)
Δ4(a,b,0,0,..)
Δ5(..,a,b-b,a)
Pmma
Pcc2
Pmc2$_1$
Γ4-(a,0,0)
I4$_1$md
Γ5-(a,0,0)
I$\bar{4}$2d
Pmm2
X1(0,0,0,0,a,b)
Γ3(a,0)
Γ5-(0,a,-a)
I4$_1$/amd
Imma
Ima2
Cm
X1(a,b,c,d,c,d)
X2(0,0,a,b,-a,-b)
X3(0,a,b,c,-b,c)
X4(a,0,b,c,b,-c)
Cc
Γ1(a)
Γ5(a,0,0)
Γ4-(a,a,b)
Pnna
X2(0,0,0,0,0,a)
Cm
C2/c
Fd-3m
Γ3-(a,0)
I-4m2
F-43m
Γ2-(a)
C2/m
Γ5(a,a,a)
R-3m
Γ5(a,b,b), Γ4(a,0,-a)
Pmna
Cm
W1(..,a,b-a,-b)
W2(..,a,b,a,b)
X3(0,0,0,0,0,a)
Pnma
X4(a,0,0,0,0,0)

Fig. 2

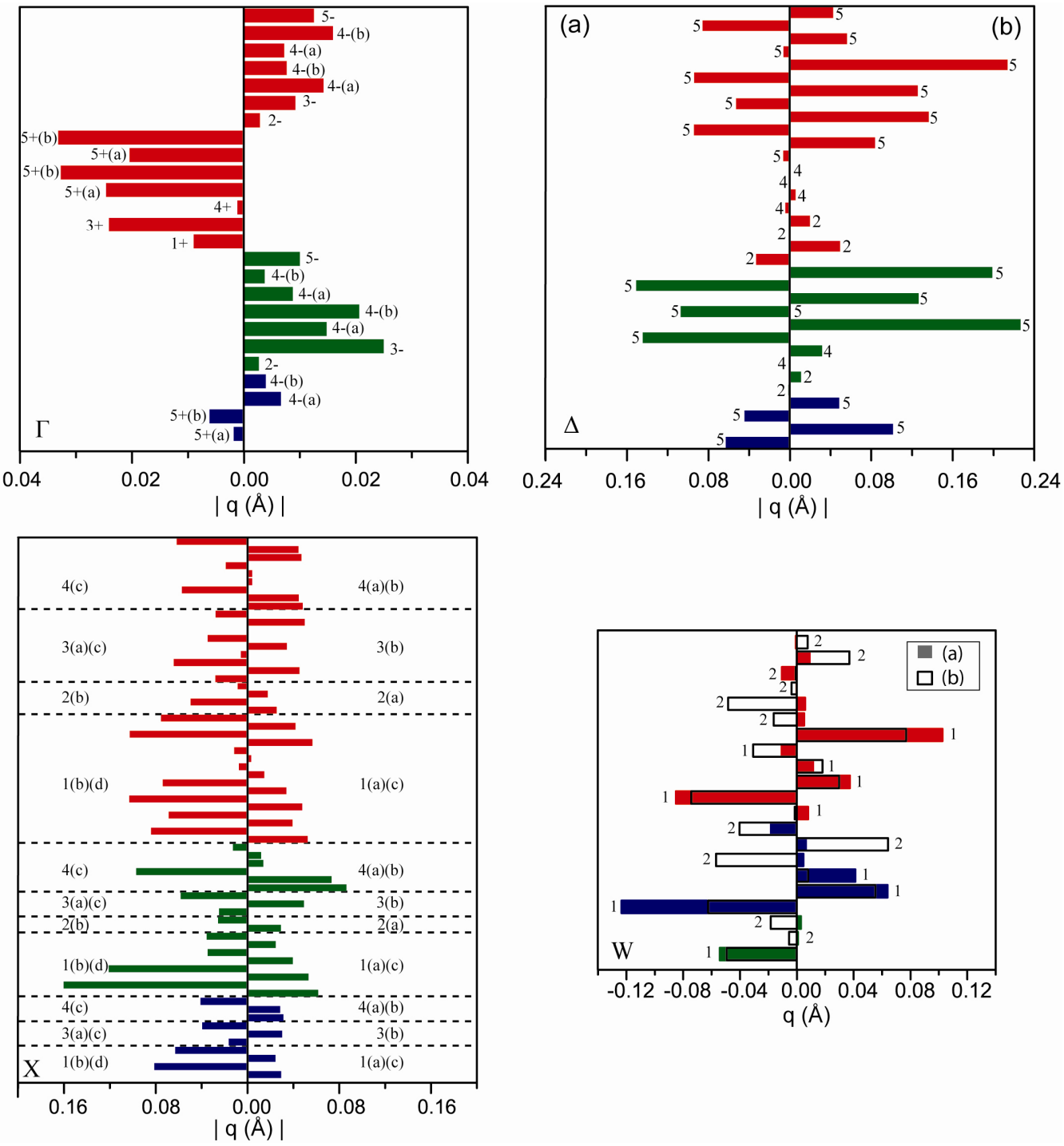
Γ
5-
4-(b)
4-(a)
4-(b)
4-(a)
3-
2-
5+(b)
5+(a)
5+(b)
5+(a)
4+
3+
1+
5-
4-(b)
4-(a)
4-(b)
4-(a)
3-
2-
4-(b)
4-(a)
5+(b)
5+(a)
0.04 0.02 0.00 0.02 0.04
| q (Å) |
(a)
(b)
Δ
0.24 0.16 0.08 0.00 0.08 0.16 0.24
| q (Å) |
X
4(c)
4(a)(b)
3(a)(c)
3(b)
2(b)
2(a)
1(b)(d)
1(a)(c)
0.16 0.08 0.00 0.08 0.16
| q (Å) |
W
(a)
(b)
-0.12 -0.08 -0.04 0.00 0.04 0.08 0.12
q (Å)

Fig. 3